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TIME-RESOLVED SPECTROSCOPIC STUDIES OF SURFACE REACTIONS.(U)

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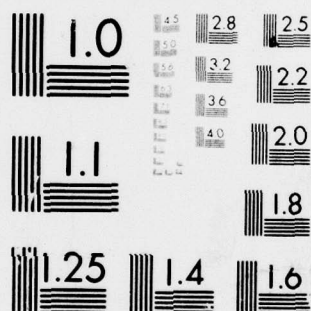
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TIME-RESOLVED SPECTROSCOPIC STUDIES OF SURFACE REACTIONS**

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ABSTRACT

A new dynamic approach to the study of surface reactions is described. A fast-acting UHV gas dosing system is employed to prepare the adsorbate in an initial state under reaction conditions of elevated temperature and/or pressure (to ~ 1 torr). Individual reaction steps are then resolved in time using photoemission spectroscopy to probe the surface electronic structure, yielding information about the nature of chemisorbed species, the reaction path, and the kinetics of individual reaction steps. Preliminary results are given for an initial application of this approach - the measurement of desorption kinetics for CO on Ni(111).

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1. Introduction

In recent years electron spectroscopic techniques (photoemission, electron energy loss, etc.) have provided valuable insight into the nature of chemisorbed species and the reaction paths of these species on the surface. For surface reactions involving molecular adsorbates from the gas phase, the combination of ultraviolet photoemission spectroscopy (UPS) and flash desorption mass spectroscopy (FDMS) has proven especially rewarding. The case of methanol (CH_3OH) decomposition on Ni(111) surfaces¹ serves as a useful example of this approach. FDMS is employed to determine particular "transformation" temperatures at which the reaction proceeds fairly quickly (a few sec. or shorter) through specific reaction steps which involve desorption products and to identify these products. UPS provides a picture of the density of occupied electron states in the surface region ($\sim 10\text{-}15\text{\AA}$ deep), revealing the identity of surface species and often the mechanism for their chemical bonds to the surface. As shown schematically in Fig. 1, the reaction is then investigated by heating the surface to the various "transformation" temperatures in order to drive it through these reaction steps and studying the nature of surface species after each step by UPS. This approach constitutes an essentially static study of the reaction which utilizes temperature-processing. Such static studies typically involve adsorption phases formed at low pressure ($\lesssim 10^{-6}$ torr) and reaction steps initiated at the lowest possible temperatures.

This approach leaves unanswered two questions which have practical significance as well as fundamental interest:

1. What are (a) the nature of chemisorbed species and (b) the surface reaction pathways at higher temperatures and higher gas pressures?
2. What are the kinetics and energetics of the various steps in the reaction?

We have developed an alternative, dynamic approach for spectroscopic studies of surface reactions which has the potential to answer both these questions. In it, reaction steps are resolved in time under conditions of elevated surface temperature and incident gas pressure, situations closer to practical reaction conditions. In the following this approach is described and some preliminary results are given for a simple test reaction.

II. Time-Resolved Approach

Time-resolved studies of surface reactions are achieved here by (1) first preparing surface species in an initial condition at elevated sample temperature and elevated reactant gas pressure and (2) then measuring the time-evolution of the surface species under these reaction conditions using surface-sensitive spectroscopies, especially UPS. The initial condition is produced by a brief exposure of the clean surface (held at elevated temperature) to the reactant gas using a fast-acting UHV gas dosing valve. The time-evolution of the UPS spectrum after the dose then contains information on the nature of chemisorbed species, the surface reaction path, and the kinetics of various reaction steps.

Consider the schematic example of a simple reaction in Fig. 2, in which the reactant exposure from the gas dosing system produces an initial adsorbate phase A which then reacts to form a second phase B. The UPS measurements can be considered in two ways:

1. Spectral dependence. By measuring the UPS spectrum of the surface species within some time window, one can determine the nature of chemisorbed species formed under these reaction conditions after a particular reaction time. The sequence of species observed reveals the reaction path.

2. Time dependence. By monitoring the time-evolution of parts or all of the UPS spectrum for a given phase, the kinetics (rate constants) of the preceding or following reaction step are measured. Activation energies Δ and pre-exponential (frequency) factors K_0 for these rate constants are then deduced from the temperature dependence of these rate constants $K(T) = K_0 \exp(-\Delta/kT)$. It is clearly desirable to measure the kinetics over as wide as possible a range of sample temperatures (or equivalently, reaction times).

III. Experimental Techniques

The key to time-resolution of surface reaction steps is the fast-acting gas dosing valve. It is an UHV bakeable device fully compatible with the vacuum quality of the surface spectroscopy system. The valve is differentially pumped and consists of multiple stages of blades which either cover or leave open a series of small apertures between the gas load chamber and the sample. It is switched on (open) or off (closed) by a fast-acting solenoid outside the vacuum, which drives a bellows and thereby the

internal moving parts. The switching time of the valve is 2-3 msec, so that exposure times as short as a few msec are readily achieved, with adjustable duty cycle. The dynamic range of measurable reaction times thus extends to potentially 10^6 , from $\sim 10^{-2}$ sec to $\sim 10^4$ sec, the time for significant contamination in the UHV system.

The conductance of the valve is ~ 3 ml/sec on and $\sim 3 \times 10^{-3}$ ml/sec off. Since the local pressure at the sample surface P_{samp} is determined by gas flow through the valve in either position, $P_{\text{samp}}^{\text{on}}/P_{\text{samp}}^{\text{off}} \approx 10^3$. Furthermore, the actual valve portion of the dosing system is located close to the sample, with a short nozzle after the valve to direct the gas onto the surface at the focal point of the electron spectrometer; this produces an enhancement of P_{samp} compared to the residual gas pressure P_{sys} in the UHV chamber $P_{\text{samp}}/P_{\text{sys}} \approx 10^2$, independent of valve position. An auxiliary solenoid-operated valve makes it possible to pump out the gas load chamber quickly (< 0.5 sec) for cases when measurements are to be done for reaction times much longer than the dosing time. As a result, the gas exposure during the on time can be kept much greater ($\sim 100\times$) than the accumulated exposure during the off time.

The enhancement $P_{\text{samp}}/P_{\text{sys}} \approx 10^2$ and the large system volume (~ 150 l) make it possible to inject a brief dose of gas at relatively high pressure (~ 1 torr) and then carry out electron spectroscopy on the absorbed species so formed. For example, with a load chamber pressure of 250 torr and an on time of 10 msec, the sample surface sees a local gas pressure of 0.6 torr with a total exposure of 6000 langmuirs. At the end of this dose $P_{\text{sys}} \sim 5 \times 10^{-5}$ torr, so that the electron multiplier can be left on and electron spectroscopy measurements can be made immediately following the dose (the local P_{samp} above the surface decreases to $\sim P_{\text{sys}}$ in < 1 msec). Higher pressures may be possible with experimental improvements, particularly differential pumping of the electron multiplier.

High counting rates available in UPS provide the possibility of measuring a significant portion or all of the UPS spectrum in a short time (≤ 100 msec). With hot filament operation of the He resonance lamp, counting rates of order 10^6 sec^{-1} have been achieved for adsorbate molecular orbital features at ~ 0.3 eV resolution. This would give 3% statistics for a 50 point spectrum taken in 50 msec. Data is acquired directly into the computer using the analog input module of a device coupler² at rates as fast as 0.7 msec per (x,y) point.

IV. CO/Ni(111) Desorption Kinetics

As an initial test of this time-resolved reaction study approach, we have measured the kinetics of desorption of molecularly chemisorbed CO from Ni(111). The isosteric heat of adsorption for this system has previously been determined from adsorption isosteres $\log p_{\text{CO}}$ vs. T^{-1} at various coverages (measured by work function change $\Delta\phi$) by Christmann et. al.³ These measurements were carried out over the temperature range $23 < T < 164^\circ\text{C}$; surface carbon produced by the disproportionation reaction $2\text{CO} \rightarrow \text{C}_{\text{ads}} + \text{CO}_2\uparrow$ prevented such measurements above 164°C . The results show a coverage-dependent activation energy for desorption which varies from ~ 30.0 kcal/mole (~ 1.30 eV) at low θ to ~ 23.5 kcal/mole (~ 1.02 eV) near saturation.

We monitored the intensity of the UPS signal at the $5\sigma/1\pi$ adsorbate orbital (~ 8 eV below the Fermi energy) and thereby measured the temperature-dependence of the desorption rate. We assume that changes in the UPS signal are proportional to coverage changes of chemisorbed CO (approximately true from our studies). The data were taken with the more common cold-cathode operation of He resonance lamp, which gave lower counting rates than mentioned in the previous section.

The time-dependence of the UPS signal for sample temperature $T = 175^\circ\text{C}$ is shown in Fig. 3 for a 200 msec dose after a 100 msec delay (curve a), followed by a 300 msec dose after a similar delay (curve b). The CO coverage (taken as proportional to the UPS signal) saturates in ~ 50 msec, as seen clearly by comparing the two curves. Fairly rapid desorption (in ~ 250 msec) is then observed following the dose because the sample temperature is near that of the flash desorption peak. Both curves in Fig. 2 represent averages of 13 successive runs. The amplitude of the UPS intensity change is somewhat smaller in the second set because the disproportionation reaction has poisoned (filled) some of the surface sites for CO chemisorption at this temperature. Because data can be obtained even for a single dosing cycle, this time-resolved approach is viable even when competing reactions (like disproportionation in this case) occur with similar rates. This represents a significant advantage for studies of the desorption reaction compared to the adsorption isostere approach,³ in which a single measurement involves many adsorption-desorption cycles.

Similar data for the desorption of CO at various temperatures from 122°C to 227°C is shown in Fig. 4. A change in desorption rate is clearly observable for only $\sim 10^\circ\text{C}$ change in sample temperature. The ability of the time-resolved approach to

overcome the problem of competing, surface-poisoning reactions is shown in the higher temperatures of these measurements compared to previous work.³

For a first analysis of data like that in Fig. 4, we assume a simple first-order desorption mechanism

$$\theta(t) = \theta_0 e^{-K_{DES}t} = \theta_0 e^{-t/\tau_{DES}} \quad (1)$$

where the temperature-dependent desorption rate constant is given by

$$K_{DES}(T) = K_0 e^{-\Delta/kT} \quad (2)$$

where Δ is the activation energy for desorption (\approx heat of chemisorption) and K_0 is the pre-exponential (frequency) factor. If we assume K_{DES} is coverage-independent and deduce it simply from the $\frac{1}{e}$ time of the desorption curves (like those in Fig. 4), we obtain the data points shown by circles in Fig. 5. They give $K_0 \approx 1 \times 10^{13} \text{ sec}^{-1}$ and $\Delta \approx 25 \text{ kcal/mole} \approx 1.08 \text{ eV}$.

The results of Christmann et. al.³ are indicated in the inset in Fig. 5 and show a coverage-dependent Δ with $K_0 \approx 1 \times 10^{13} \text{ sec}^{-1}$. They find that $\Delta \approx 30 \text{ kcal/mole}$ at very low θ and $\Delta \approx 23.5-26.5 \text{ kcal/mole}$ for most of the coverage range. The temperature-dependence of K_{DES} is also shown by straight lines for three values of Δ in the range found by Christmann et. al. Note that the new data plotted here agrees with that corresponding to a Δ value averaged over the coverage range from the results of Christmann et. al.³.

The coverage-dependence of the desorption rate constants can in fact be seen directly in the desorption curve at a single fixed temperature, as illustrated in Fig. 6 for $T = 162^\circ\text{C}$. Here the experimental data is shown together with calculated θ -independent first-order desorption curves for various K_{DES} values. The measured curve is clearly not a simple single exponential, but instead K_{DES} changes with coverage.

In a more complete analysis of such data, the coverage-dependent desorption rate constants

$$K_{DES}(T, \theta) = - \frac{1}{\theta} \frac{d\theta}{dt} \quad (3)$$

can be calculated from the desorption curves. Plots of K_{DES} vs. $\frac{1}{T}$ at various θ will then reveal Δ and K_0 for various coverages. This analysis is presently in progress.

V. Conclusions

As illustrated in the example of CO desorption from Ni(111), the time-resolved reaction study approach described here provides a way to measure directly the kinetics of individual surface reaction steps. This can be done even if the step involves no desorption products. It can be employed even in the presence of competing reactions. Furthermore, it gives a way to investigate the surface reaction at elevated temperature and/or pressure (closer to reaction conditions) and to reveal the nature of chemisorbed species present under such conditions. Finally, it will extend the utility of electron spectroscopies to much higher pressure (~ 1 torr) than previously obtainable (10^{-5} – 10^{-4} torr), so that new adsorbate interactions and reaction paths may be observed.

VI. Acknowledgement.

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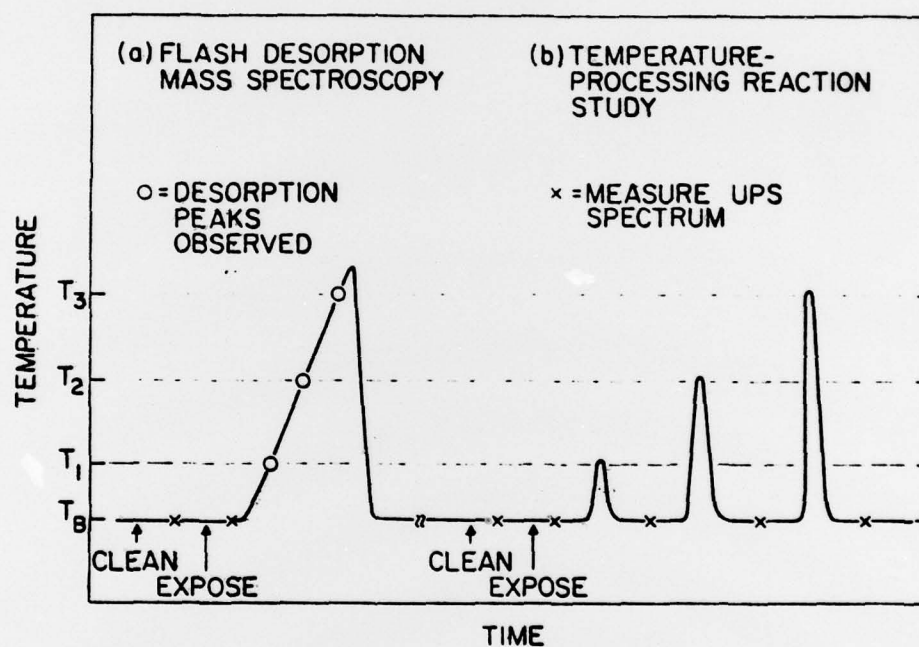


Fig. 1

Schematic illustration of static reaction study approach using temperature-processing. After initial gas exposure at some low base temperature T_B .

(a) FDMS is used to determine temperatures T_1 , T_2 , T_3 , ... at which desorption products are observed. The surface is then cleaned and another initial gas exposure is made. In a temperature-processing study

(b), the UPS spectrum is measured before and after the gas exposure and after successive heating (and recooling) cycles to temperatures T_1 , T_2 , T_3 , ...

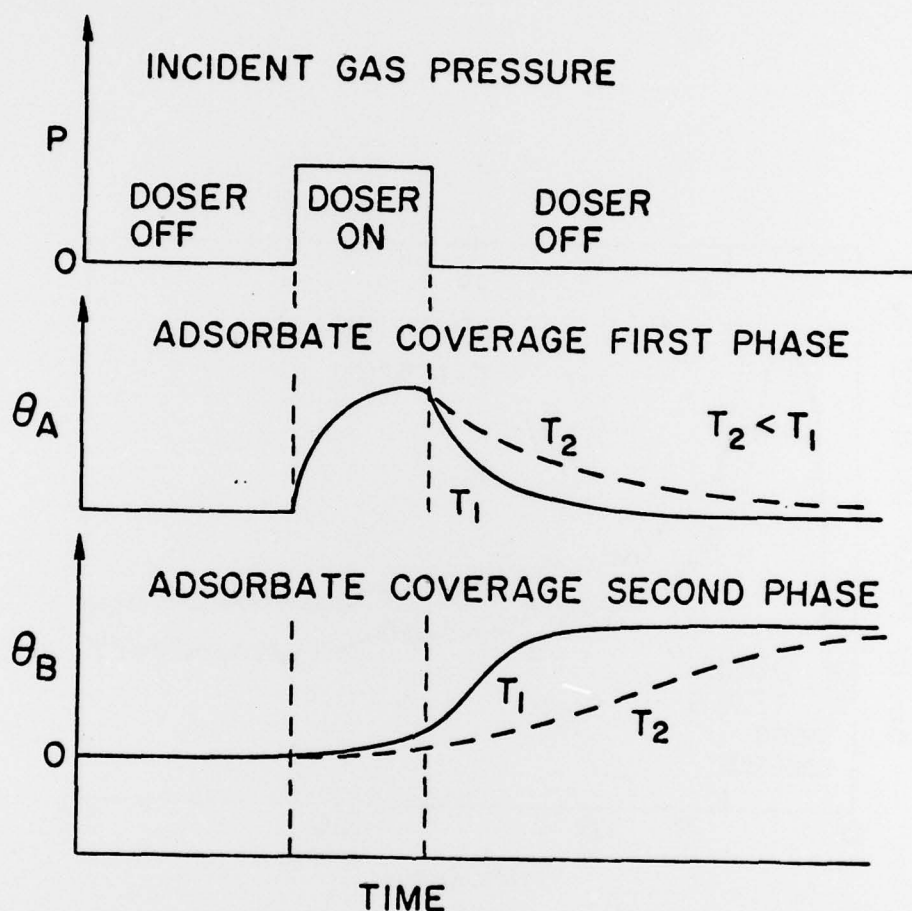


Fig. 2

Schematic example of time-resolved surface reaction. (a) Gas dosing system produces exposure during doser on-time. (b) This produces coverage θ_A of initial adsorbate phase (possibly up to saturation). θ_A then decays in time after the dose with rate determined by sample temperature T_1 as surface species A converts to second adsorbate phase species B. (c) Coverage θ_B of species B grows correspondingly in time. At a lower temperature $T_2 < T_1$, this conversion time is longer.

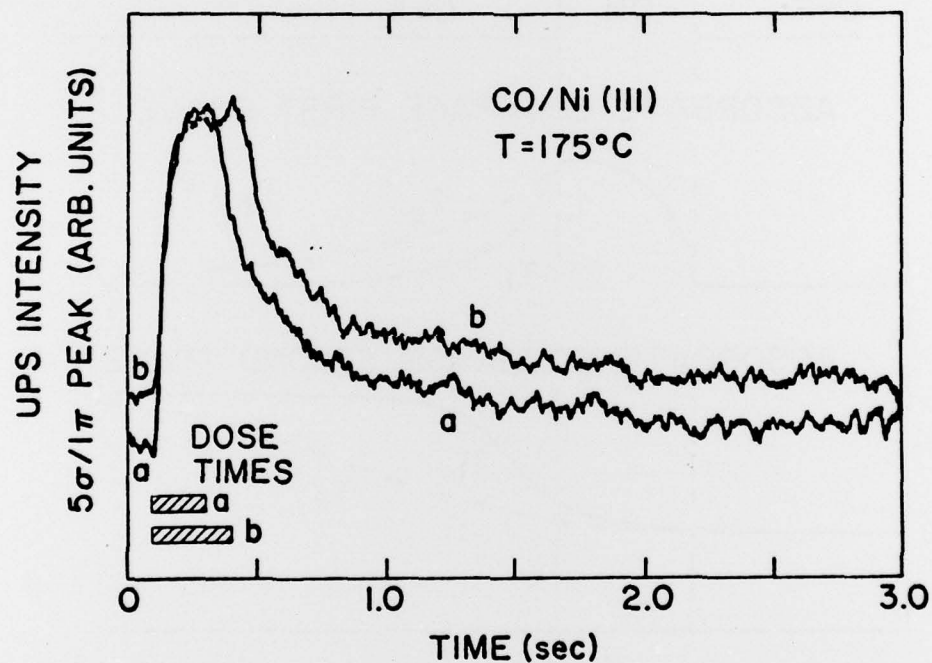


Fig. 3 Adsorption/desorption of CO on Ni(111) at 175°C due to 200 msec dose (curve a) after 100 msec delay and 300 msec dose (curve b) after similar delay. The photoemission intensity of the CO 5σ/1π molecular orbitals is taken as proportional to the coverage of chemisorbed CO.

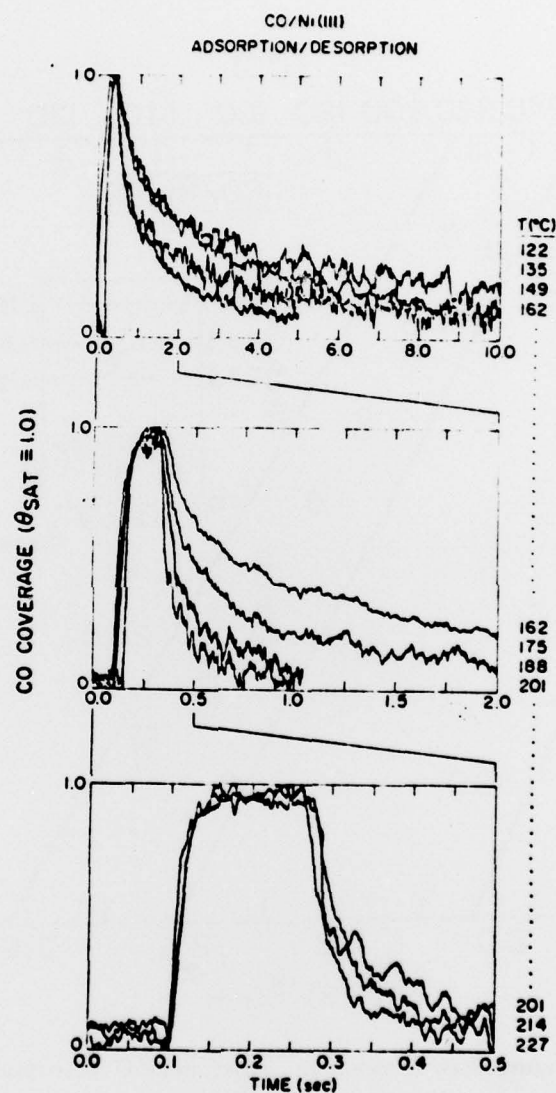


Fig. 4

Adsorption/desorption of CO on Ni(111) at various temperatures due to 150 msec dose after 100 msec delay. The CO coverage (with saturation coverage defined as $\theta_{\text{SAT}} = 1.0$) is obtained from the UPS intensity at the CO $5\sigma/1\pi$ orbital peak.

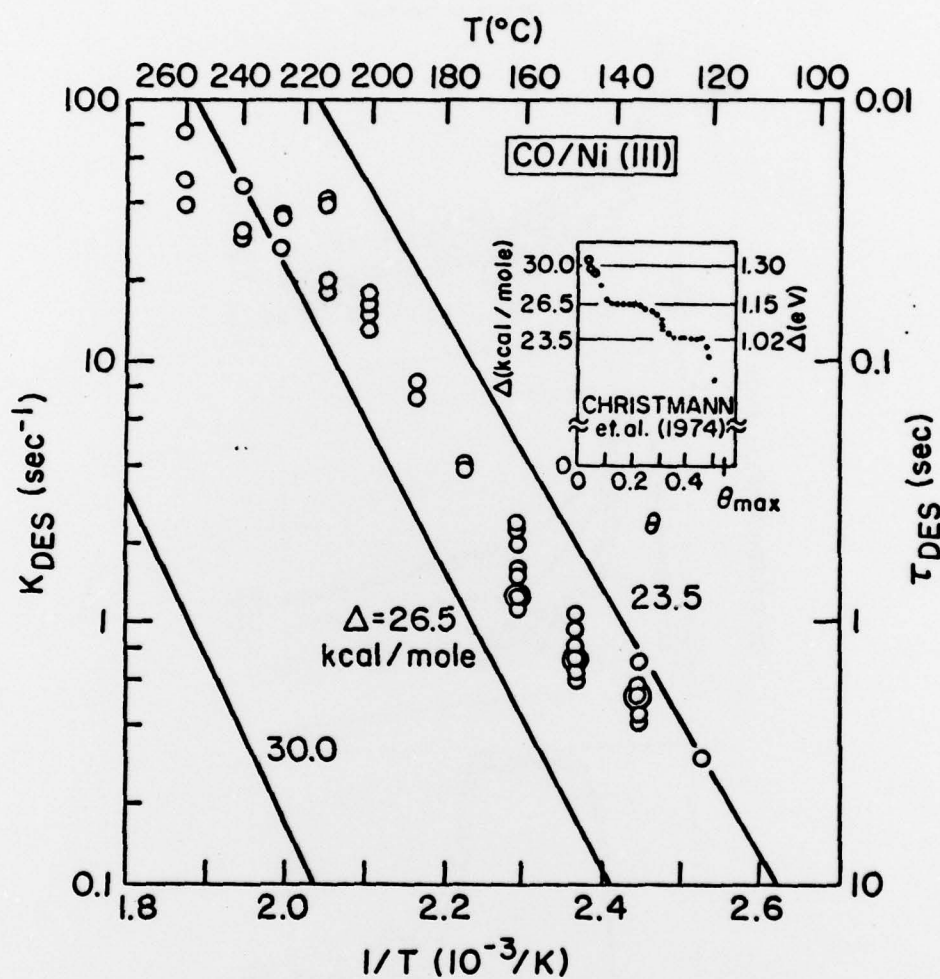


Fig. 5 Temperature-dependence of experimental desorption rate (circles) determined by assuming coverage-independent rate constants and using $\frac{1}{\tau}$ time of desorption curves. Insert reproduces the previous results of Christmann et. al. (Ref. 3); three of these Δ values give the straight lines shown for K_{DES} vs. $\frac{1}{T}$.

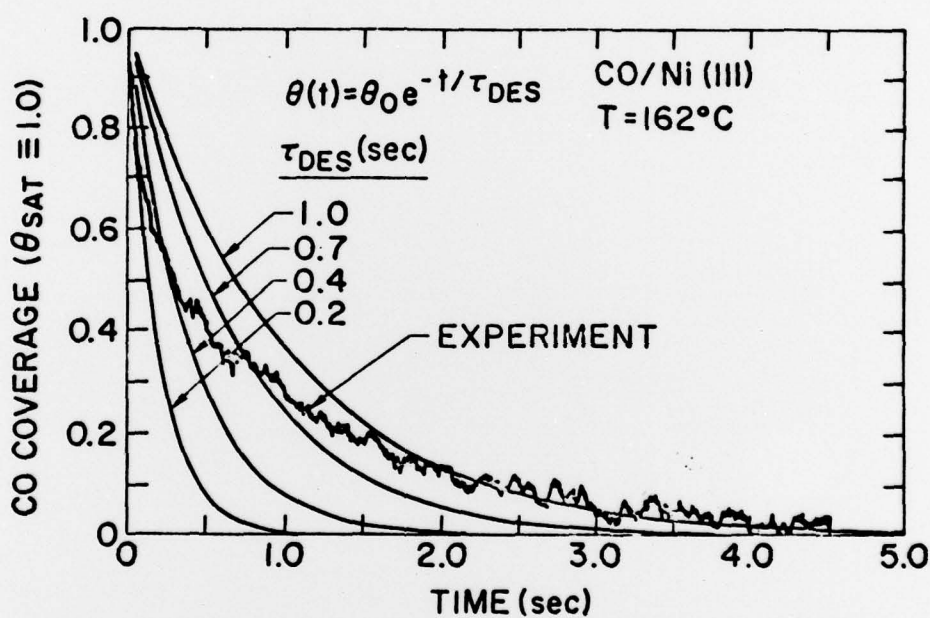


Fig. 6

Experimental desorption curve for $T = 162^\circ\text{C}$ and calculated exponential curves corresponding to simple coverage independent first-order desorption rate constants.

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